Model-free determination of interatomic distance by using a new mathematical XAFS oscillation analysis

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Introduction

  In the most fundamental analysis of x-ray absorption fine structure (XAFS), i.e., radius distribution function (RDF) determination of an element selected by absorption edge, the Fourier transform (FT) of the XAFS oscillation is well known to provide a shorter interatomic distance than the actual one. The shorter estimation is caused by ignoring phase shift in photoelectron scattering. We normally estimate the interatomic distance by using fitting of a theoretical calculation assuming a local structure model to the experimental XAFS oscillation. The posteriori analytical process means insufficient ability to characterize unknown materials. In this report, a model-free analysis for estimation of interatomic distance is proposed.

Experimental methods

  The reason for shorter estimation of interatomic distance indicates that if the phase shift is determined somehow, basis functions including the phase shift can adopt for a linear regression to the experimental XAFS oscillations, resulting in an actual atomic distance. Note that a linear regression using basis excluding the phase shift corresponds to the conventional FT. Importantly, the solution considering the phase shift should provide a Gauss distribution consistent with an existence probability of thermally vibrating atom. Now, we consider an inverse problem: in order that the RDF has high symmetry consistent with the Gauss distribution, we determine the phase shift. The inverse problem can be solved with a recursive procedure, namely (1) preset an appropriate phase shift, (2) a linear regression of XAFS oscillation with basis functions including the preset phase shift, (3) evaluation of the symmetry of the RDF, and (4) if the RDF is asymmetric, then go to (1). Consequently, RDF with the highest symmetry can be obtained self-consistently with the algorism, and the most probable interatomic distance is determined from the RDF. The linear regression was performed with LASSO (Least Absolute Shrinkage and Selection Operator) which is useful for the sparse modeling that deconvolutes overlapping peaks and reduces noise.

Results and discussions

  The experiments to confirm the validity of this new technique were performed for randomly selected 35 ceramics. For comparison between conventional and the proposed analyses of the selected ceramics, XAFS database for the standard materials on SPring-8 experimental data repository was used. For an evaluation of accuracy, interatomic distances calculated from lattice constants and crystal structures on literatures were used as a benchmark. It was found that the conventional FT analysis provided the shorter estimation up to -25 %, while the new technique indicated more accurate distance within ±6 %. In addition to this physical accuracy, advantage of the proposed technique is insensitivity to chemical properties: We necessary to identify neither the chemical component nor crystal structure prior to the analysis. In fact, the randomly selected ceramics for the analyses included various compounds such as alloys, halogens, and oxynitrides.

Conclusions

A model-free XAFS analysis in which recursively retrieve phase shift in photoelectron scattering was developed. Although conventional analysis using Fourier transform provided a shorter interatomic distance, the proposed technique indicated a reasonable distance with higher accuracy. This technique was insensitive to chemical properties, and so was applicable to various compounds.